IS 354-6 (1989): Methods of sampling and test for resins for paints, Part 6: Special test methods for amino resins [CHD 20: Paints, Varnishes and Related Products]

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IS 354 (Part 6) : 1989
(Reaffirmed 2002)

Indian Standard

RESINS FOR PAINTS — METHODS OF SAMPLING AND TEST

PART 6 SPECIAL TEST METHODS FOR AMINO RESINS

(Second Revision)

भारतीय मानक

रंग रोगनों के लिए रेज़िन — नमूने लेने की और परीक्षण-पद्धतियाँ

भाग 6 एमिनों-रेज़िनों के लिये विशेष परीक्षण-पद्धतियाँ

(दूसरा पुनरीक्षण)

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BUREAU OF INDIAN STANDARDS
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Price Group 2

FOREWORD

This Indian Standard (Second Revision) was adopted by the Bureau of Indian Standards on 1 August 1989, after the draft finalized by the Raw Materials for Paint Industry Sectional Committee had been approved by the Chemical Division Council.

This standard was originally published in 1952 covering methods of sampling and general test methods mainly for natural resins. Subsequently, an Indian Standard for methods of sampling and test for natural and synthetic resins was published as Part 2 of this standard, in 1971. These two parts were amalgamated and revised in 1976. The present revision has been necessitated as more and more newer synthetic resins, such as polyamides, polyvinyls and emulsion polymers are being manufactured and used in the country. While revising the standard, the Committee felt it appropriate to publish this standard in various parts, as indicated below:

Part 1 General test methods
Part 2 Special test methods for alkyd resins
Part 3 Special test methods for phenolic resins
Part 4 Special test methods for epoxy resins
Part 5 Special test methods for polyamide resins
Part 6 Special test methods for amino resins, and
Part 7 Special test methods for acrylic and vinyl acetate resins and emulsions

In this standard (Part 6) test methods covered in **19.1** to **19.4** of IS 354 : 1976 'Methods of sampling and test for resins for paints (*first revision*)' have been included. In addition, identification test for free urea, urea-formaldehyde and melamine-formaldehyde and determination of free formaldehyde test have also been added.

In the formulation of this standard, assistance has been derived from ISO/DIS 9020 'Binder for paints and varnishes — Determination of free formaldehyde content in amino resins — Sodium sulphite titrimetric method', issued by the International Organization for Standardization (ISO).

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

RESINS FOR PAINTS — METHODS OF SAMPLING AND TEST

PART 6 SPECIAL TEST METHODS FOR AMINO RESINS

(Second Revision)

1 SCOPE

This standard (Part 6) prescribes the special test methods for amino resins used in paints and enamels.

2 REFERENCES

The following Indian Standards are necessary adjuncts to this standard:

IS No.	*Title*
IS 265 : 1976	Specification for hydrochloric acid (*second revision*)
IS 517 : 1967	Specification for methanol (methyl alcohol) (*first revision*)
IS 1117 : 1975	Specification for one mark pipettes (*first revision*)
IS 1303 : 1983	Glossary of terms relating to paints (*second revision*)
IS 1997 : 1982	Specification for burettes (*second revision*)
IS 2263 : 1979	Methods of preparation of indicator solution (*first revision*)
IS 2316 : 1968	Methods of preparation of standard solutions for colorimetric and volumetric analysis (*first revision*)
IS 5194 : 1969	Method for determination of nitrogen-Kjeldahl method
IS 6667 : 1972	Glossary of terms used in synthetic resin industry

3 TERMINOLOGY

3.1 The definitions given in IS 1303 : 1983 and IS 6667 : 1972 shall apply.

4 SAMPLING

Representative samples of the amino resins shall be drawn as prescribed in **3** of Part 1 of this standard.

5 IDENTIFICATION

Mix a small amount of material with 2 ml of 72 percent (*v*/*v*) sulphuric acid and a few crystals of chromotropic acid and heat by keeping test-tube in a beaker of water at 60 to 70°C for 10 minutes. A bright violet colouration indicates the presence of amino resins.

5.1 Colour Test to Identify Melamine-Formaldehyde Resin

5.1.1 *Reagents*

5.1.1.1 *Concentrated hydrochloric acid, see* IS 265 : 1976.

5.1.1.2 *Congo paper*

5.1.1.3 *Sodium thiosulphate crystals*

5.1.1.4 *Hydrogen peroxide solution*, 3 percent.

5.1.2 *Procedure*

5.1.2.1 Place 1 to 2 g of amino resin in ignition tube. Add a few drops of concentrated hydrochloric acid to the contents of the tube. Heat to 190°C to 200°C in a glycerine bath. Place congo paper in the mouth of the ignition tube during heating. Continue heating till congo paper placed in the mouth of the tube does not turn blue. Cool the content and add a few crystals of sodium thiosulphate. Moisten congo paper in 3 percent hydrogen peroxide and place in the mouth of tube. Heat the contents to 160°C in glycerine bath and observe colour of congo paper.

5.1.2.2 If melamine-formaldehyde resin is present then congo paper will turn blue.

NOTE — Free melamine also responds to this test.

5.2 Precipitation Test to Identify Free Melamine in Melamine-Formadehyde Resin

A small portion of melamine resin is boiled in aniline. A white precipitate if formed, which is soluble in water, indicates the presence of free melamine in melamine-formadehyde resin.

5.3 Precipitation Test to Identify Urea-Formaldehyde Resin

5.3.1 *Reagents*

5.3.1.1 *Acetic acid solution*, 20 percent.

5.3.1.2 *Xanthydrol solution*, 1 percent solution in methanol.

5.3.1.3 *Pyridine*

5.3.2 *Procedure*

5.3.2.1 Weigh 0·05 g of the amino resin in a 250-ml round bottom flask. Add 25 ml of 20 percent acetic acid solution and reflux for half an hour. Cool and filter the solution through a filter paper. Collect 10 ml of the filterate in an evaporating dish. Add to this 0·2 to 1 ml of 1 percent xanthydrol solution in methanol. Evaporate the mixture to dryness on a water bath. Transfer the residue to a small test tube and add a few drops of pyridine. Warm gently the test tube and dissolve the residue.

5.3.2.2 If urea-formaldehyde resin is present then crystals of urea xynthydrol (small needle split or tapered at the ends) are obtained on cooling.

NOTE — Free urea also responds to this test.

5.4 Spectroscopic Method to Identify Different Resins

The absence of bands at 6 μm (principally due to amide carbonyl group) and the presence of a band 12·2 μm spectra of resin may be taken as good evidence of melamine resin. The presence of a band at 6 μm shows the presence of urea.

6 DETERMINATION OF TOTAL NITROGEN

6.1 Outline of the Method

The nitrogen in amino resin is determined by Kjeldahl method.

6.2 Procedure

Weigh accurately a quantity of the material that will contain 150 to 250 mg of nitrogen, using a weighing tube if the material is a liquid and transfer to a digestion flask. Proceed and calculate the percentage of nitrogen as prescribed in IS 5194 : 1969.

7 DETERMINATION OF TOTAL FORMALDEHYDE

7.1 Outline of the Method

The material is distilled. The distillate is treated with hydrogen peroxide and sodium hydroxide and titrated against hydrochloric acid after refluxing.

7.2 Reagents

7.2.1 *Phosphoric Acid*, 1 : 1 (*v*/*v*).

7.2.2 *Methyl Red Indicator*, *see* IS 2263 : 1979.

7.2.3 *Hydrogen Peroxide Solution*, 100 volumes.

7.2.4 *Sodium Hydroxide Solution*, approximately 0·1 N.

7.2.5 *Phenolphthalein Indicator Solution*, *see* IS 2263 : 1979.

7.2.6 *Standard Hydrochloric Acid*, 0·1 N.

7.3 Procedure

Weigh accurately 0·2 g of the sample into a 100-ml round-bottom flask fitted with a side arm for a thermometer. Add 20 ml of phosphoric acid and connect the flask to a distillation assembly having provision for addition of water during distillation. Distil with suitable water additions to maintain the liquid temperature between 115 and 120°C. Collect 150 ml of the distillate. Add 5 ml of hydrogen peroxide and minimum quantity of sodium hydroxide solution to neutralise the distillate using methyl red indicator and heat for 30 minutes under reflux. Cool and titrate with standard hydrochloric acid. Carry out a blank determination using all the reagents except the material.

7.4 Calculation

$$\text{Total formaldehyde, percent by mass} = \frac{(V_1 - V_2) \times N \times 0{\cdot}3}{M}$$

where

V_1 = volume in ml of standard hydrochloric acid used in blank titration,

V_2 = volume in ml of standard hydrochloric acid used in the titration with the material,

N = normality of the standard hydrochloric acid, and

M = mass in g of the material taken for test.

8 DETERMINATION OF FREE FORMALDEHYDE

8.1 Outline of the Method

Free formaldehyde and of formaldehyde hydrate are reacted with excess sodium sulphite solution at 0°C to form hydroxymethane sulphonate. The excess sodium sulphite is titrated with iodine solution. The hydroxymethane sulphonate is decomposed with sodium carbonate solution and the liberated sodium sulphite is titrated with iodine solution.

8.2 Reagents

8.2.1 *Sodium Sulphite Solution*, 1 N.

8.2.2 *Acetic Acid*, 1 N.

8.2.3 *Sodium Carbonate Solution*, 10 percent.

8.2.4 *Buffer Solution*

Dissolve 12.37 g of boric acid in water in a 1 000-ml one-mark volumetric flask, add 100 ml of a 1 N sodium hydroxide solution, dilute to the mark with water and mix well. Before use, cool the solution to 0°C.

8.2.5 *Standard Iodine Solution*, 0·05 N (*see* IS 2316 : 1968).

8.2.6 *Dichloromethane Neutral*

Before use, cool the dichloromethane to 0°C.

8.2.7 *Starch Solution*, 10 g/l.

8.2.8 *Ice Water*

8.2.9 *Ice*

8.3 Apparatus

8.3.1 *High-Speed Mixer*

8.3.2 *Magnetic Stirrer*

8.3.3 *Ice Bath*, maintained at 0°C.

8.3.4 *Burettes, see* IS 1997 : 1982.

8.3.5 *Pipettes, see* IS 1117 : 1975.

8.4 Procedure

8.4.1 *Test Portion*

By reference to Table 1, select the appropriate mass of the test portion to be taken. If the free formaldehyde content cannot be predicted, take a test portion of about 1 g. Weigh, to the nearest 0·001 g, and transfer to a 600 ml beaker.

Table 1 Selection of Test Portion for Determination of Free Formaldehyde

Expected Free Formaldehyde Content	Mass of Test Portion
percent (m/m)	g
Up to 0·5	3
Above 0·5 to 1	1·5
Above 1 to 2	1
Above 2 to 3	0·5
Above 3 to 5	0·25

8.4.2 *Determination*

Carry out the determination in duplicate. Ensure that the temperature of the contents of the beaker is kept at 0°C during the whole determination. If necessary, add some ice to the mixture. In the case of water-soluble products, dissolve the test portion immediately in a mixture of 150 ml of the ice water, about 10 g of the ice and 25 ml of the buffer solution. In the case of products that do not form clear solutions with water, dissolve the test portion immediately in 50 ml of dichloromethane. Then add a mixture of 150 ml of the ice water, about 20 g of the ice and 25 ml of the buffer solution and emulsify with the high-speed mixer for 10 seconds. Withdraw the mixer and rinse it with a small volume of the ice water.

8.4.2.1 Place the beaker in the ice bath and stir the contents of the beaker, using the magnetic stirrer. Whilst continuously stirring, add, by means of a burette, 2 ml of the sodium sulphite solution. Continue stirring for 15 minutes and add 10 ml of the acetic acid and 3 or 4 drops of the starch solution. Titrate with the iodine solution until a greyish-blue or violet coloration is obtained that is stable for at least 10 seconds. Then add 30 ml of the sodium carbonate solution. Titrate the liberated sodium sulphite with the iodine solution until a blue colouration is obtained that is stable for at least 1 minute. Record the volume (V) of the iodine solution required for this titration.

8.5 Calculation

Calculate the free formaldehyde content, using the equation:

$$= \frac{V \times N \times 0{\cdot}0015}{m} \times 100$$

where

V = volume in mm of the iodine solution,

N = normality of standard iodine solution, and

m = mass in g of the test portion.

9 DETERMINATION OF TOTAL UREA

9.1 Outline of the Method

The method determines urea content by spectrophotometry in butylated urea-formaldehyde resin solutions and in mixtures of such urea and melamine resins. The resin is hydrolyzed in methanolic hydrochloric acid and the urea condensed with *p*-dimethyl-aminobenzaldehyde to develop a yellow colour, the intensity being a measure of the urea content.

9.2 Apparatus

9.2.1 *Spectrophotometer*

A suitable spectrophotometer employing essentially monochromatic light shall be required.

9.2.2 *Absorption Cells*

Matched absorption cells with 1·0 cm light path shall be required.

9.2.3 *Flask and Condenser*, 100-ml round-bottom flask fitted with 300-mm water condenser shall be required.

9.2.4 *Pipette*, Lunge's type, of 2 ml capacity.

9.3 Reagents

9.3.1 *Ehrlich's Reagent*

Weigh 2·0 g of *p*-dimethyl-aminobenzaldehyde into a beaker of 100 ml capacity. Add nearly 70 ml of 95 percent (*v*/*v*) ethanol and 10 ml of hydrochloric acid. Stir well. Filter, if necessary, into a 100-ml volumetric flask and dilute to the mark with 95 percent ethanol.

9.3.2 *Methanol*, conforming to IS 517 : 1967.

9.3.3 *Methanolic Hydrochloric Acid*

Add 200 ml of methanol to a volumetric flask of 500 ml capacity. Add by pipette 50 ml of hydrochloric acid to flask, dilute to mark with methanol and mix.

9.3.4 *Standard Urea Solution*

Dissolve 0·1 g of urea in methanolic hydrochloric acid in a 200-ml volumetric flask, make up to mark with methanolic hydrochloric acid and mix well.

9.4 Procedure

Weigh to the nearest 0·1 mg, 0·10 ± 0·01 g of resin solution containing approximately 23 to 26 percent urea. Add from a pipette 10 ml of methanol and 1·0 ml of hydrochloric acid. Add a few pieces of pumice or glass beads and attach the condenser and reflux for 2 hours. Cool and wash the condenser with a few millilitre of methanolic hydrochloric acid. Transfer completely to a 50-ml volumetric flask, dilute to the mark with methanolic hydrochloric acid and mix. From this point, the testing should be carried out simultaneously on the sample, a standard and a blank. A double quantity of blank is required for cell corrections. Arrange in order 50-ml, 25-ml and 25-ml flasks for blank, standard and sample respectively. Pipette out 20-ml of methanolic hydrochloric acid into the flask for blank, 10-ml of standard urea solution into the flask for the standard and sample and 10-ml of Ehrlich's reagent into the flask for the blank and 5 ml into each of the other flasks. Dilute each flask to the mark with water. Mix, let stand for 1 hour. Filter only the sample through a fine textured filter paper. Transfer the blank, standard and test sample solutions to 1·0 cm absorption cells and fit in the spectrophotometer. Allow 10 minutes to get temperature equilibrium. Measure the absorbance at 420 nm using a slit width of 0·15 mm. Replace the solutions in the standard and test sample cells with blank solution and measure the absorbance of the solutions in each cell after 10 minutes equilibrium period, to get cell corrections. Apply these corrections to the standard and test sample solution readings.

9.5 Calculation

$$\text{Total urea, percent by mass} = \frac{A_s \times U \times 25}{A_u \times M}$$

where

A_s = corrected absorbance of the test sample solution,

U = mass in g of urea in 200 ml of standard solution,

A_u = corrected absorbance of the standard urea solution, and

M = mass in g of the material taken for test.

Bureau of Indian Standards

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Review of Indian Standards

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